

POOR QUALITY

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO ELECTRODES

(71) We, SIEMENS AKTIENGESellschaft, a German company, of Berlin and Munich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an electrode suitable for the anodic oxidation of a liquid fuel, e.g. hydrazine, dissolved in an electrolyte, and to a process for the preparation of the electrode.

Fuels dissolved in an electrolyte may be converted at the anodes of fuel cells, which anodes usually consist of a porous or non-porous support material activated on at least one side with a noble metal. For example, on page 129 of *Electrochemical Technology*, 1965, there is described a hydrazine-air fuel cell in which a sintered plate of nickel carbonyl, activated with palladium, is used as the anode.

A carbon electrode for fuel cells operated with hydrazine, in which platinum is disposed on the surface of electrode (as a catalyst) is also known from "Soviet Electrochemistry", Vol. 3 (1967), page 5.

It has been found that, with the deposition of noble metals on support materials, particularly with platinum on nickel grids or lattices, using the known processes, only a weak bond is achieved in many cases. It was observed that the platinum becomes partially detached from the support material during the electrochemical conversion and, due to the resulting poor contact, the ohmic resistance of the electrode is raised. It has also been found that platinum deposited on nickel grids has a low specific surface. Similar effects were observed when rhodium was deposited on nickel grids. Furthermore when noble metals have

a low specific surface, they are easier to contaminate.

It is therefore an object of the present invention to provide an electrode which has both a high activity and a strong bond on the support material.

According to one aspect of the present invention, there is provided an electrode suitable for use as an anode in the oxidation of a liquid fuel dissolved in an electrolyte, which electrode comprises an electrically conductive support on the surface of which is disposed porous catalytically active metal layer formed by alloying a catalytically active metal with a catalytically inactive element and subsequently dissolving out the inactive element, on which metal layer in turn is disposed a layer of a metal mixture consisting of from 10 to 30% of ruthenium and from 90 to 70% of palladium.

The metal of the porous catalytically active metal layer includes those which can be formed by fusing Ni, Co, Fe or Cu with a catalytically inactive element, e.g. Al, Si or Zn, and subsequently dissolving out the inactive element.

It is of course already known to use porous catalytically active metals in the electrodes of fuel cells which employ liquid fuels dissolved in the electrolyte, but it was surprising that, when they are used as the catalyst support, they have such a favourable influence on the properties of the palladium-ruthenium mixture, particularly when the latter is disposed on a porous nickel layer. Porous metal catalysts are characterised by a favourable steady potential and high-catalytic activity, but are very sensitive to high over-voltages and to oxygen, so that often the less sensitive noble metal catalysts were used in their place. The present inven-

tion appears to incorporate the good aspects of the porous active metals and the ruthenium-palladium mixture.

5 The production of the electrode according to the present invention may be carried out in accordance with another aspect of the present invention by a process which comprises applying a porous catalytically active metal formed by alloying a catalytically active  
10 metal with a catalytically inactive element and subsequently dissolving out the inactive element, to an electrically conductive support and then applying to the resulting porous catalytically active metal layer, a metal mixture consisting of from 10 to 30% of ruthenium and  
15 from 90 to 70% of palladium.

The porous active metal layer may be formed by depositing electrolytically an alloy of the active metal and an inactive metal on  
20 an electrically conductive support, for example a grid or plate consisting of, e.g. carbon, graphite or a metal, especially nickel and V<sub>2</sub>A-steel. When, for example, the active metal is nickel, mixtures of nickel and zinc salt solutions are used as a starting solution. Particularly good bonds are produced on  
25 nickel grids or lattices when the electrodeposition solution containing, say, 10% by weight of NiSO<sub>4</sub>, 3% of ZnSO<sub>4</sub> and 10% of (CH<sub>3</sub>COO)<sup>-</sup>Na and the deposition is carried out within 10 minutes at a current density of 50 mA./cm.<sup>2</sup> at 60°C. Firmly adhering metal alloy layers may also be deposited from, for  
30 example, an electrodeposition solution containing, say, 5% by weight of NiSO<sub>4</sub>, 5% by weight of ZnSO<sub>4</sub>, 5% by weight of NH<sub>4</sub>Cl and 10% by weight of NH<sub>4</sub>OH, at 20°C. The current density in this case was also 50 mA./cm.<sup>2</sup>.

40 The composition of the electrodeposition solution and the deposition conditions are obviously not restricted to those given by way of example; thus, the deposition can also take place at current densities of from, for example,  
45 10 to 200 mA./cm.<sup>2</sup>. The alloy of the catalytically active metal and the catalytically inactive element can also be applied by other known processes to the electrically conductive support material, for example, by means of  
50 a vapour-coating or flame-spraying process, and the bond strength can also be increased by a subsequent tempering in a protective gas atmosphere, e.g. nitrogen, at 300 to 700°C. In most cases, however, the bonding strength  
55 is so great that such after-treatment is unnecessary.

The application of the active metal alloy by flame-spraying, hereinafter referred to as plasma-spraying, may be effected using argon, containing hydrogen and/or nitrogen, as the  
60 spraying gas. The hydrogen or nitrogen content may be 3 to 10% by volume, but it is advantageously from 4 to 6% by volume.

65 The spraying of active metal alloys by means of a plasma burner is already known.

but in this known process, a gas mixture consisting of hydrogen and oxygen is used as the burner gas. However, pure hydrogen or pure nitrogen are not completely suitable as  
70 the spraying gas for the application of the alloys. In order to produce a good bonding strength, it has proved to be advantageous to provide the plasma spraying plant with an inert gas, e.g. argon, spray which prevents  
75 access of oxygen from the ambient atmosphere.

The activation of the applied alloy may be effected in a manner known *per se* by introduction into an aqueous alkali metal hydroxide solution, e.g. 6N KOH, followed possibly by  
80 treatment with an aqueous solution of hydrochloric acid and ferric chloride in order to stabilise and increase the activity.

Preferably, the ruthenium-palladium catalytic layer is deposited without any electric current. It has been found to be expedient as regards the activation process to  
85 dissolve out only that quantity of the catalytically inactive component of the metal alloy that will leave a quantity available which is equivalent to the subsequent ruthenium-palladium mixture to be deposited.

Alternatively, the hydrogen stored in the active metal or the active metal itself can be used for the currentless ruthenium-palladium deposition. However, the latter deposition can, like the previous deposition of the metal alloy, also take place electrolytically.

Since the specific surface of the ruthenium-palladium deposited on the porous active metal is very great, a high catalytic activity is obtained with very small quantities of ruthenium and palladium. Thus, in a solution of 6N KOH and 0.5M hydrazine at 20°C, excellent current-voltage curves were obtained  
100 when employing 1 mg. of a palladium-ruthenium mixture per square centimetre.

The porous active metal may also be directly applied to the support material, by firstly dipping the grids or plates into a suitable adhesive solution, e.g. a dispersion of polytetrafluoroethylene, and thereafter coating the dipped support with active or stabilised porous active metal powder.

Porous nickel is the preferred porous metal since it appears to give more satisfactory results than, say porous cobalt.

For a better understanding of the present invention and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings, in which:—

Figure 1 shows graphically the current-voltage characteristics of an electrode of the present invention and three other electrodes;

Figures 2, 3 and 4 show graphically the current-voltage characteristics of electrodes of the present invention as well as other electrodes;

Figure 5 shows graphically the characteris-

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tics of a fuel cell in which the anode was in accordance with the present invention;

Figure 6 shows graphically the current-voltage characteristics of another electrode according to the present invention;

Figures 7 and 8 are cross-sections through different electrodes according to the present invention; and

Figure 9 is a cross-section through a fuel cell in which the anode is the electrode of Figure 8.

Figure 1 shows the current-voltage curves plotted in a half-cell using electrodes according to the present invention. A Hg/HgO electrode was used as a reference electrode in this case, and also in each of the following examples. A 6N KOH solution, with which 0.5M hydrazine had been admixed, was used as the electrolyte. The catalytic electrode included in each case a nickel grid, on to which the alloy had been deposited electrolytically from a solution containing 10% of NiSO<sub>4</sub>, 3% of ZnSO<sub>4</sub>, and 10% of (CH<sub>3</sub>COO) Na at 60°C. and 50 mA./cm<sup>2</sup>. The alloy was activated prior to noble metal deposition. The noble metal content of the catalytic electrodes was 1 mg./cm<sup>2</sup>, in each case.

The deposition of the noble metals or noble metal mixtures was effected either without current by being dipped into a deposition bath or electrolytically at 30 mA./cm<sup>2</sup>. With the electrode of which the characteristics are shown in curve 1, the bath consisted of 0.05% of RhCl<sub>3</sub> and 0.2% of PdCl<sub>2</sub>, with that of curve 2, of 0.03% of IrCl<sub>3</sub> and 0.18% of PdCl<sub>2</sub>, with that of curve 3 of 0.2% of PdCl<sub>2</sub>, and with that of curve 4 of 0.03% of RuCl<sub>3</sub> and 0.15% of PdCl<sub>2</sub>. Curves 1, 2 and 3 are included for comparative purposes.

The results of comparison tests obtained under the same conditions as in Figure 1 are shown in Figure 2. Here curve 5 corresponds to the curve 4 shown in Figure 1. In curve 6 there are shown the current-voltage values of an electrode in which the same ruthenium-palladium mixture was directly deposited on the nickel grid or lattice. Comparison of curves 5 and 6 shows that the activity of the noble metal catalytic mixture is considerably improved by the intermediate layer of porous nickel.

Oddly enough, only a slight increase in activity was produced with an electrode in which the noble metal layer applied to the porous nickel consisted of platinum, compared with platinised grid electrodes. It might be assumed from this result that other reciprocal effects occur between the Pd/Ru mixture and the porous nickel. Curve 7 illustrates the characteristics of a platinised nickel grid electrode and curve 8 shows the characteristics of an electrode in which an intermediate layer of porous nickel was disposed between the

Figure 3 shows the advantage obtainable with electrodes according to the present invention, compared with known porous nickel electrodes. Here curve 10 corresponds to the curve 4 in Figure 1 and curve 9 shows the characteristics of an electrode in which a support was provided with a porous nickel layer, but which was not provided with a noble metal layer.

The behaviour of electrodes according to the present invention was investigated over relatively long operational times and compared with the behaviour of a platinised nickel grid electrode. The results are shown in Figure 4.

Curve 11 is for the case when the porous nickel intermediate layer was coated with a mixture of palladium and ruthenium (3:1), curve 12 for when it was coated with palladium, curve 13 for when it was coated with platinum, and curve 14 is for a platinised nickel grid electrode. Curves 12, 13 and 14 are included for comparative purposes. The current loading during the measurements was 30 mA./cm<sup>2</sup>. The potential of the electrodes with an intermediate layer of porous nickel (curves 11, 12 and 13) remains almost constant or only slightly tends to the positive over a period of 7 days, whereas the potential of the platinised nickel grid electrode (curve 14) increases by about 155 mV. after only 24 hours.

With the results shown in Figure 5, an electrode according to the present invention, catalysed with a palladium/ruthenium mixture, was tested in a fuel cell. The electrolyte consisted of 6N KOH and 0.5M N<sub>2</sub>H<sub>4</sub>·OH. A porous silver powder electrode having 400 mg. of Ag/cm<sup>2</sup> was used as the cathode. The potential of the anode measured against a Hg/HgO reference electrode is plotted in curve 15 and the potential of the cathode in curve 16. Curve 17 shows the cell voltage, which even at 100 mA./cm<sup>2</sup> is 0.75V. and which is about 200 mV. higher than the voltage obtained under the same test conditions with a known grid electrode without any porous nickel.

In another test, a nickel grid formed from wires having a thickness of 0.15 mm. was cleaned with trichloroethylene and thereafter pickled in chromosulphuric acid. After washing, a Ni-Al alloy (50:50) with a grain size of <50μm was applied to both sides of the cleaned grid by means of a plasma burner.

The spraying gas consisted of 95% by volume of argon and 5% by volume of hydrogen. The operating current of the arc in the spraying plant was 300A and the voltage drop was 50V. The spraying plant was provided with an argon sprinkler, so that neither the nickel grid nor the components of the Ni-Al alloy became oxidised. The small molten particles of the Ni-Al alloy formed an alloy with the nickel grid, and conse-

tween the ni-Al alloy and the nickel grid, which is still present after activation of the Ni-Al alloy using a 6N KOH solution. Then 5 mg. of a mixture consisting of palladium and ruthenium (4:1 by weight) were deposited per square centimetre on the resulting porous nickel layer.

The current-voltage characteristic of the resulting electrode is shown in Figure 6. The values were measured in an electrolyte of 6N KOH and 0.5M  $N_2H_4OH$  at 20°C. by comparison with a Hg/HgO reference electrode.

Figures 7 and 8 each show a catalytic electrode according to the present invention.

In Figure 7, the electrode consists of a metallic support 18, e.g. a sheet of nickel, on which is deposited a porous nickel intermediate layer 19 and a catalytic layer 20 consisting of a palladium - ruthenium mixture. Instead of the non-porous support 18, there may be employed a nickel grid 21, as shown in Figure 8, on which is disposed a porous nickel layer 22 and a palladium - ruthenium catalyst 23.

In the fuel cell shown in Figure 9, a catalytic electrode according to the present invention is used as the anode. The fuel cell comprises closure plates 24, 25 and nickel grids 26, 27 functioning as spacers. The cathode 28 is separated from the anode 29 (of the type shown in Figure 8) by a diaphragm 30 which is impervious to gas in the electrolyte-impregnated state. The oxidising agent is supplied through a conduit 31 and the electrolyte containing the fuel through a conduit 33. The discharge of the unconsumed reactants takes place through conduits 32 and 34.

#### WHAT WE CLAIM IS:—

1. An electrode suitable for use as an anode in the oxidation of a liquid fuel dissolved in an electrolyte, which electrode comprises an electrically conductive support on the surface of which is disposed a porous catalytically active metal layer formed by alloying a catalytically active metal with a catalytically inactive element and subsequently dissolving out the inactive element, on which metal layer in turn is disposed a layer of a metal mixture consisting of from 10 to 30% of ruthenium and from 90 to 70% of palladium.

2. An electrode as claimed in Claim 1, wherein the catalytically active metal is nickel.

3. An electrode as claimed in Claim 1, wherein the catalytically active metal is copper, iron or cobalt.

4. An electrode as claimed in Claim 1, 2 or 3, wherein the electrically conductive support is formed of nickel.

5. An electrode as claimed in Claim 1, substantially as hereinbefore described with reference to any one of curves 4, 5, 10 and 11 of Figures 1 to 4, Figure 5 and Figure

6, or with reference to, and as illustrated in, Figure 7 or 8 of the accompanying drawings.

6. Process for the production of a catalyst electrode as claimed in any one of Claims 1 to 4, which comprises applying a porous catalytically active metal formed by alloying a catalytically active metal with a catalytically inactive element and subsequently dissolving out the inactive element, to an electrically conductive support and then applying to the resulting porous catalytically active metal layer, a metal mixture consisting of from 10 to 30% of ruthenium and from 90 to 70% of palladium.

7. Process according to Claim 6, wherein the porous catalytically active metal layer is formed by depositing the catalytically active metal and zinc electrolytically on the support from an aqueous solution of the catalytically active metal and zinc salts, and dissolving the zinc wholly or partially out of the resulting metal alloy on the support with subsequent activation.

8. Process according to Claim 6, wherein the porous catalytically active metal layer is formed by plasma spraying an alloy of the catalytically active metal and a catalytically inactive metal onto the support, a mixture of an inert gas and hydrogen and/or nitrogen being used as the spraying gas, and wholly or partially dissolving out the inactive metal of the metal alloy.

9. Process according to Claim 8, wherein the hydrogen and/or nitrogen content in the gaseous mixture is from 3 to 10% by volume.

10. Process according to Claim 9, wherein the hydrogen and/or nitrogen content in the gaseous mixture is from 4 to 6% by volume.

11. Process according to Claim 8, 9 or 10, wherein the inert gas is argon.

12. Process according to Claim 6, wherein the porous catalytically active metal is applied to the support with an adhesive.

13. Process according to any one of Claims 6 to 12, wherein the mixture of ruthenium and palladium is deposited non-electrolytically.

14. Process according to any one of Claims 6 to 12, wherein the mixture of ruthenium and palladium metal is deposited electrolytically.

15. Process according to Claim 6, substantially as hereinbefore described with reference to any one of curves 4, 5, 10 and 11 of Figures 1 to 4 and Figures 5 to 8 of the accompanying drawings.

16. An electrode whenever prepared by the process claimed in any one of Claims 6 to 15.

17. A fuel cell, wherein the anode is an electrode as claimed in any one of Claims 1 to 5 and 16.

18. A fuel cell as claimed in Claim 17,

substantially as described with reference to,  
and as shown in, Figure 9 of the accom-  
panying drawings.

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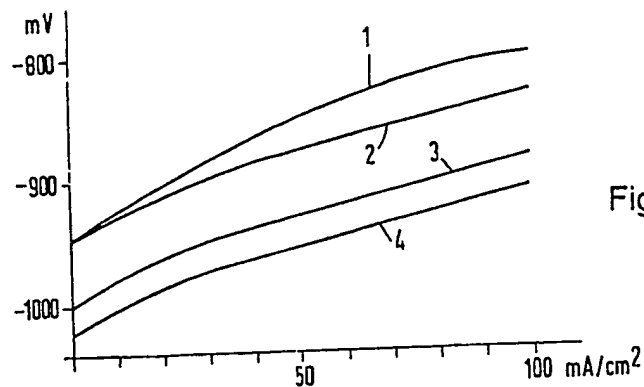


Fig. 1

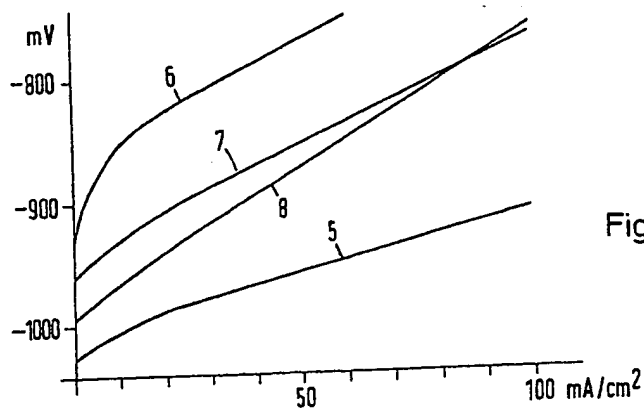


Fig. 2

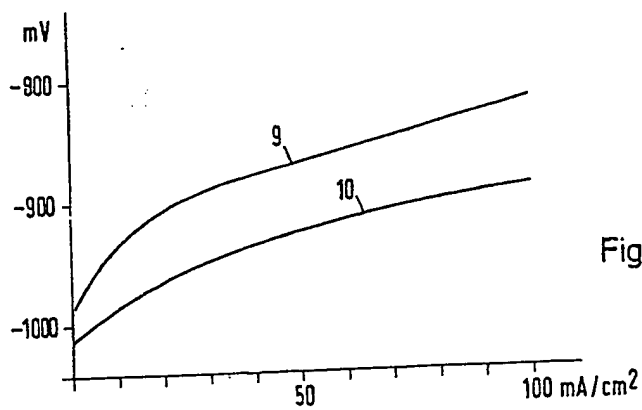


Fig. 3

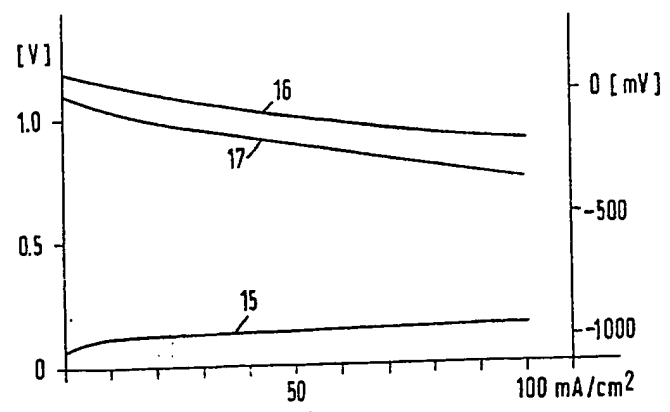
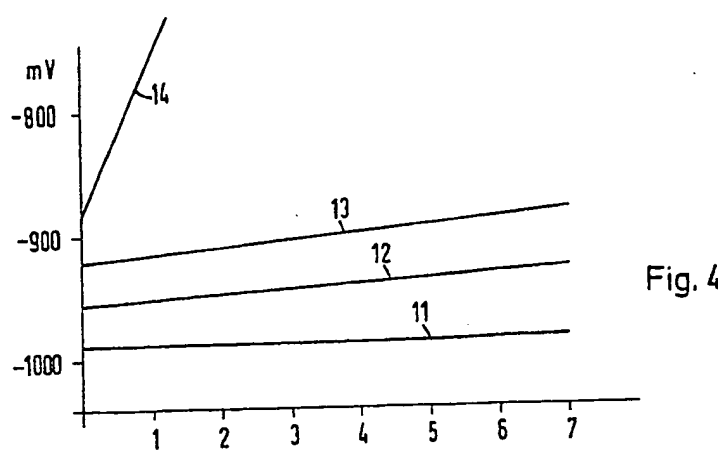


Fig. 5

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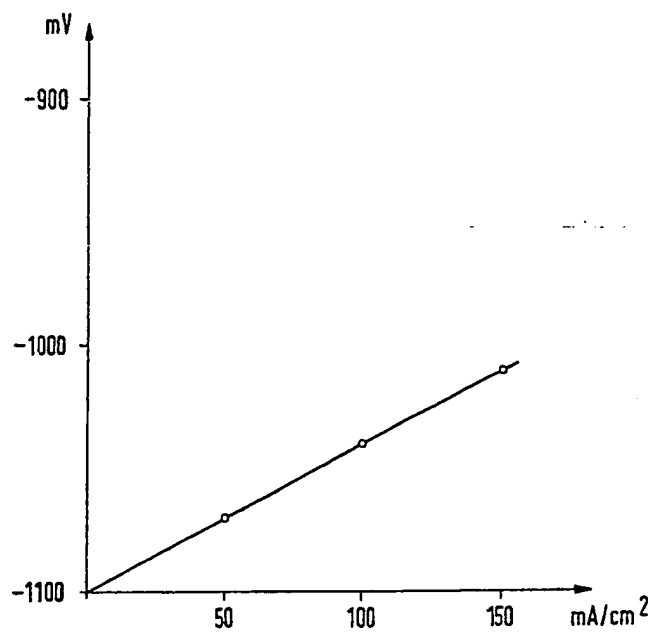


Fig. 6



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Sheet 4

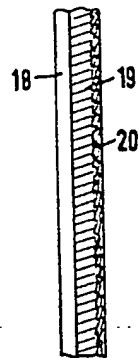


Fig. 7

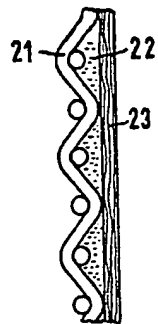


Fig. 8

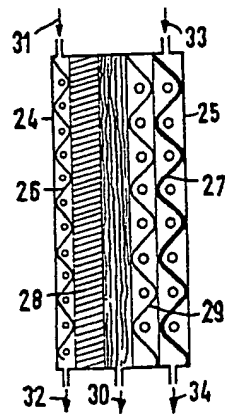


Fig. 9